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**TECHNICAL REPORT No. 8**

**INTERFACIAL CHEMICAL REACTIONS OF Au WITH  
III-V COMPOUND SEMICONDUCTORS**

by

**C.T.Tsai, J.H. Pugh and R. Stanley Williams**

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July, 1988

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**INTERFACIAL CHEMICAL REACTION OF Au WITH  
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**ABSTRACT**

The solidus portions of the nine Au-III-V (III = Al, Ga, In; V = P, As, Sb) ternary phase diagrams at 298K have been determined. Many of the solid-phase equilibria were found by calculating reaction enthalpies directly from thermochemical data available in the literature. However, for some systems, no data were available, and the required data were estimated or experiments were performed to determine the tie lines through the ternaries. Ideal conditions (no vapor-phase formation or significant mutual solid solubility) were assumed. The resulting phase diagrams may be used to determine, in systems that are effectively closed, which metal/semiconductor interfaces in the Au-III-V family are stable and which are not.

X-ray photoelectron diffraction studies

## I. INTRODUCTION

→ In order to understand the chemistry at the interface between two solids, one must first know the thermodynamic stability of the bulk materials with respect to each other. When the system involves three elements, such as a gold thin film on a III-V compound-semiconductor substrate, a ternary phase diagram must be determined. The application of ternary phase diagrams in order to understand thin oxides on III-V materials has been discussed by Schwartz et al.,<sup>1</sup> and the interaction of oxygen and nitrogen with various thin metal films on Si has been examined by Beyers.<sup>2</sup> More recently, the authors of this paper have shown that chemical reactions observed to occur at Au/GaAs<sup>3</sup> and Au/InP<sup>4</sup> interfaces can be understood quite well in terms of the relevant ternary phase diagrams, which in turn can be used to predict what metallic phases will be stable with respect to the compound semi-conductors.<sup>5,6</sup> Beyers, et al., have developed a useful classification scheme for reactive vs. nonreactive systems based on the form of the ternary phase diagram.<sup>7</sup>

Even though phase diagrams are crucial for understanding the chemistry of complex systems, only a few ternary phase diagrams have been reported involving metals used as contacts with the elements of the compound semiconductors. Such phase diagrams may be determined experimentally,<sup>1,3</sup> but the investigations are tedious and time-consuming. Thus, the ability to calculate ternary phase diagrams is highly desirable. However, very few of the thermochemical data necessary for such calculations have been



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determined experimentally, making it necessary to augment the existing heats of formation and absolute entropies with accurate estimates of the missing values.

Once the necessary thermochemical values have been obtained, phase diagrams can be constructed and subsequent experiments performed to eliminate any ambiguities present as a result of uncertainties in the available data. Because all the elements and their respective compounds considered here are in the condensed phase at room temperature and under an external pressure of one atmosphere, the ternary phase diagrams represent equilibria that may not be reached easily at lower temperatures because of kinetic factors. Metastable phases may occur and the formation of equilibrium compounds may not take place unless the systems are annealed for long times.

The most straightforward application of the bulk ternary phase diagrams to metal contacts on compound semiconductors is to determine which metals will react with the substrate. They can also be used, however, to understand the sequence of reaction products observed in thin film ( $\sim 100\text{\AA}$ ) reactions.<sup>4</sup> A discussion of the estimates of  $\Delta H^\circ_{298}$  used in calculating the phase equilibria is presented in the next section. The methods used to construct ternary phase diagrams are discussed in Section III, and the results are presented and discussed in Section IV.

## II. ESTIMATION OF THERMOCHEMICAL DATA

In two sequential papers, Miedema et al.<sup>8,9</sup> have discussed a model for estimating enthalpies of formation of transition metal alloys. This method utilizes six empirically determined parameters for each element, which are tabulated in Refs.8 and 9. A computer program is used to calculate the enthalpy of formation ( $\Delta H_{298}^{\circ}$ ) for the solid compounds and the enthalpy of mixing for the liquid phase solutions of pairs of elements, one of which must be a transition metal. The model yields satisfactory results for binary systems of two transition metals, but Miedema et al.<sup>8,9</sup> caution that it is less reliable for systems that involve a non-transition metal. Many authors, in their discussions of the chemistry at metal/compound-semiconductor interfaces, have used either the enthalpy of mixing of liquid-phase solutions or  $\Delta H_{298}^{\circ}$  of intermetallic compounds taken from the tables in Refs.8 and 9. For the case of intermetallic compounds of Au with the group-III metals, the agreement between the model of Miedema et al. and the existing experimental  $\Delta H_{298}^{\circ}$  data can be seen in Fig.1.

The calculated estimates in Fig.1 correctly predict the sign of  $\Delta H_{298}^{\circ}$ , and the absolute values of the enthalpies are generally very reasonable. However, for the calculations that use the model of Miedema, the extrema in the  $\Delta H_{298}^{\circ}$  versus mole fraction  $X$  plots are always near an  $X$  value of  $1/2$ , whereas for the Au/group-III compounds, the extrema are at  $X_{Au} = 1/3$ . In other words, the fluorite structure compounds  $AuAl_2$ ,  $AuGa_2$ , and  $AuIn_2$

have the largest enthalpy of formation per gram-mole of material for each series of intermetallics. This discrepancy means that the enthalpies calculated for the Au/group-III compounds with the model of Miedema et al., even when used correctly, cannot predict reliably which products will be most stable. Thus, better estimates of the relative values of  $\Delta H_{298}^{\circ}$  for the various reaction products of transition metals with group-III metals are necessary to calculate M-III-V phase diagrams.

When  $\Delta H_{298}^{\circ}$  is plotted versus  $X$  for many different systems,<sup>10</sup> the data form a fairly smooth curve. Various functions have been examined in an empirical attempt to mimic this curve. The best agreement with the experimental data was found for the sine function:

$$\Delta H(X_A) = \Delta H(X_A^C) * \sin(\pi * X_A / (2 * X_A^C)) , \quad (1)$$

where  $\Delta H(X_A)$  is  $\Delta H_{298}^{\circ}$  at the specified mole fraction of element A,  $\Delta H(X_A^C)$  is the extremum value of  $\Delta H_{298}^{\circ}$  that occurs at a mole fraction of  $X_A^C$ , and A is chosen such that  $X_A/X_A^C$  is less than or equal to one. The mole fraction  $X_A^C$  usually corresponds to the composition of the compound that has the highest melting point of all the compounds formed from two particular metals. Thus, even if the value of  $\Delta H(X_A^C)$  is not known, the relative enthalpic stabilities of a series of intermetallic compounds for which the melting points are known may be estimated. Furthermore, if  $\Delta H_{298}^{\circ}$  for any of the compounds is known, then the

enthalpies of formation for all the others may be estimated from Eq.(1).

The values of  $\Delta H(X_A)$  for the Au/group-III intermetallic compounds calculated from Eq.(1), using the known enthalpies of formation at  $X_{Au} = 1/3$ , are also shown in Fig.1. The agreement of these empirically determined enthalpies with those determined experimentally are excellent, and thus the values of  $\Delta H_{298}^{\circ}$  used in determining tie lines through the phase diagrams, as described in the next section, were those calculated using Eq.(1) and presented in Table I.

### III. PHASE DIAGRAM CONSTRUCTION

#### A. Calculations

When ternary phase diagrams are calculated for thermochemical data, general assumptions can be used to simplify the calculations while still giving useful results. To determine the thermodynamic feasibility of a reaction at constant pressure, the change of the Gibbs free energy of the system must be calculated from known thermodynamic values,<sup>11</sup> where

$$\Delta G_R = \Delta H_R - T\Delta S_R . \quad (2)$$

When ideal, closed, solid-state systems are considered in which no vapor phase is allowed to form, the contribution of the entropy of reaction ( $\Delta S_R$ ) is usually much smaller than that of the enthalpy of reaction ( $\Delta H_R$ ), and a common assumption<sup>12</sup> is that  $\Delta H_R$  may be used to predict whether a reaction will occur or not. The error in this assumption is usually not great when reactions are considered at room temperature, and when  $\Delta H_R < 0$ , the reaction is assumed to be thermodynamically favored. However, if the absolute value of  $\Delta H_R$  is on the order of 1 kcal/mole, then the entropic contribution to the solid-state reaction may become significant.

Another assumption used here is that mutual solid solubility of the compounds in one another is negligible, and therefore all tie lines through the phase diagram will be straight, or pseudo-binary. The solubility at room temperature for the systems

studied is small, although it may become appreciable at elevated temperatures. A third assumption, a consequence of the lack of information to the contrary, is that no ternary compounds are formed.

Before tie lines are determined, however, the borders of the ternary phase diagram must include the binary compounds that exist at room temperature for each of the two-component systems. For example, it is known that, in systems containing only one group-III element (Al, Ga, In) and one group-V element (P, As, Sb), only one solid-phase compound is formed. For binary systems of gold and a group-III or group-V element, many different inter-metallic compounds exist. To find which compounds are stable at 298°C, the binary phase diagrams are consulted.<sup>13-16</sup> These diagrams form the borders of the ternary phase diagrams. Tie lines connect these compounds across the major triangle of the ternary diagrams to form tie triangles. The reason that the three-component phase diagram must consist of a network of triangles is a consequence of the phase rule derived by Gibbs:<sup>17</sup>

$$f = c - p + 2 , \quad (3)$$

where  $c$  is the number of components,  $p$  is the number of phases and  $f$  is the number of degrees of freedom in the system. No more than three solid phases may coexist in equilibrium for a ternary system with the temperature and pressure arbitrarily fixed. If the composition of a system (as determined by the lever rule)

falls inside a tie triangle, the number of components at equilibrium is three. Along a tie line and at the vertices of a tie triangle, however, the number of phases at equilibrium reduces to two and one, respectively, since there are additional constraints placed on the system.

For the ternary systems under consideration, it is assumed that no vapor phase is allowed to form because of an independently specified external pressure greater than the combined vapor pressures of the solid phase. This is an idealized, closed system and it has been shown that, when vapor does form in an open system, i.e., an ultra-high vacuum chamber, the entropy change associated with the sublimation of the group-V species can drive reactions that are endothermic.<sup>11</sup>

When many compounds exist, the number of possible tie lines increases drastically. To determine which tie lines represent the system at thermodynamic equilibrium, two possible tie lines, which cross each other at some point and represent a total of four different phases, are included in an equation representing a stoichiometric chemical reaction. The two phases connected by one of the tie lines may be considered the reactants and the two phases connected by the other, the products. The equation is balanced and the enthalpies of formation for each phase are used to determine if the reaction is endothermic or exothermic. If the reaction is endothermic, the reactions are favored and the equilibrium tie line is drawn between these two phases. This method is similar to that used by Thurmond et al.<sup>17</sup> for the

ternary system O-Ga-As, and is used in principle to check all possible reactions between the phases. The tie lines are drawn such that the most stable of the possible reaction products are connected and no two tie lines cross. As a result of the assumptions that have been made and the uncertainty in the data, there may be errors in the tie lines determined in this fashion. If the absolute value of the calculated  $\Delta H_R$  is less than the estimated uncertainty for the thermochemical data that were used, approximately 5 kcal/mole, then an experiment must be performed to determine the actual tie lines. The data used to determine the tie lines are compiled in Table I.

#### *B. Experiments*

The details of the experimental procedure were reported in a previous paper.<sup>3</sup> Samples with a total mass on the order of 1 gram and stoichiometries accurate to better than one part per thousand were sealed in quartz ampoules under a vacuum of lower than  $10^{-3}$  torr. The sealed ampoules were heated to 1000°C in a resistance furnace for one week, and then cooled to room temperature at a rate of 5-10°C per hour. Filings were removed from two sides and the center of each of the samples, and were investigated with a Phillips X-ray powder diffractometer to determine the reaction products. The total time required for a complete scan (2 $\theta$  scans from 10°-100°) was three hours and the typical signal-to-noise ratio for a strong diffraction peak was 40 to 1. The composition of each sample was identified by comparing positions, shapes, and ratios of the diffraction peaks in

the powder patterns of the filings to those of standards prepared for this experiment. The  $d$  spacings of the standards were checked against a reference tabulation<sup>18</sup> to ensure that they were identified correctly. At least five diffraction peaks were observed for each of the elements or compounds that were found in the ternary systems. No evidence for ternary compounds was found in the systems studied, since all the diffraction peaks observed corresponded to elements or known binary compounds.

#### IV. RESULTS AND DISCUSSION

The results of this study are summarized in the ternary phase diagrams shown in Figs.2-4. Of these phase diagrams, the Au-Ga-As, Au-In-As, Au-Ga-Sb, and Au-In-Sb systems have been determined experimentally and discussed in a previous paper.<sup>3</sup> For the Au-Ga-As and Au-In-As systems, the phase diagrams calculated from the values of  $\Delta H$  in Table I were in complete agreement with the experimentally determined systems. For the Au-Ga-Sb system, the pseudobinary cuts determined from the calculation of  $\Delta H$  were consistent with those from experiments except for the  $\text{AuSb}_2$ -GaSb cut, which was favored by 3.1 kcal/mole GaSb over the AuGa-Sb cut in the temperature range from room temperature to 600°C. This composition is in an experimentally uncertain region, in which four phases were found, of the phase diagram.<sup>3</sup> For the Au-In-Sb system, the calculated tie lines were different from the experimental results at the InSb-AuSb<sub>2</sub> and AuIn-AuSb<sub>2</sub> cuts, which were calculated to be more stable than AuIn-Sb by -1.1 and -3.7 kcal/mole, respectively. However, by experiment, AuIn-Sb was found to be pseudobinary and  $\psi$ -Sb was preferred.

For the Au-In-P system, the results from calculation of  $\Delta H$  were in slight conflict with experiment, since the  $\epsilon, \epsilon'$ -InP and  $\epsilon, \epsilon'$ -Au<sub>2</sub>P<sub>3</sub> cuts were preferred by  $\Delta H$ . For the Au-Al-P and Au-Al-As systems, the results yielded such large magnitudes for the  $\Delta H$  values that no experiments were performed. For the Au-Al-Sb system, the experiments showed that AuAl-AuSb<sub>2</sub> was a stable pseudobinary, whereas AlSb-AuSb<sub>2</sub> was slightly favored in the calculations of  $\Delta H$ .

Of the nine III-V compounds considered in this work, only AlP, AlAs, GaP, and GaAs are stable with respect to Au in a closed system. These four compounds have the most negative free energies of formation except for InP, which is 2 kcal/mole more stable than GaAs. Au reacts with InP because both Au-In and Au-P compounds can be formed, whereas Au does not react with GaAs because there are no stable Au-As compounds. For the same reason, the Au-InP reaction produces a more In-rich intermetallic compound with Au ( $\delta$ ) than the Au-InAs reaction, which produces  $\epsilon$ . Because of the small magnitudes of  $\Delta G_R$  for the III-Sb compounds, -11.3, -9.3, -6.1 kcal/mole, respectively, for III=Al, Ga, and In, the phase diagrams of these binaries with Au are similar. Au reacts with the III-Sb's to form an Au-III intermetallic compound and elemental Sb.

## V. CONCLUSIONS

The solidus equilibria in nine phase diagrams in the Au-III-V family have been determined by calculations involving known and estimated enthalpies of formation. Calculations of enthalpies of reaction can be used to find most of the pseudobinary tie lines. If the values of  $\Delta H$  have a small magnitude, then experiments need to be performed to determine the actual tie lines in the ternary systems, since the enthalpy values have an uncertainty, and entropy effects may be important. If anything is apparent from the nine phase diagrams in Figs. 2-4, it is that each system is unique. None of the compound semiconductors containing In or Sb is stable with respect to elemental Au. In most cases, the primary reaction is between Au and the group-III element. However, for InP, none of

the Au-In intermetallics has a large enough Gibbs free energy of formation to account completely for the reaction of Au with InP. Au and InP react because the Gibbs free energy of formation of  $\text{Au}_2\text{P}_3$  is just large enough, when combined with the formation of the Au-rich intermetallic compounds with In, to proceed at the expense of Au and InP. The phase diagrams show that Au is a completely unacceptable contact metal for AlSb, GaSb, InSb, InAs, and InP if one wishes to avoid chemical reactions at the metal/semiconductor interface.

## VI. ACKNOWLEDGMENTS

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## FIGURE CAPTIONS

- FIG. 1 - The enthalpy of formation of the Au-group-III intermetallic compounds (in kcal/g-atom) as a function of the mole fraction  $X$  of Au. The solid lines are the estimates from the model of Meidema et al.<sup>8,9</sup> The symbols are the experimental data, and the dashed lines are the empirical estimates from Eq.(1).
- FIG. 2 - Solidus portions of the ternary phase diagrams for the Au-Al-V's at 25°C.
- FIG. 3 - Solidus portions of the ternary phase diagrams for the Au-Ga-V's at 25°C. The dashed lines in the Au-Ga-Sb diagram represent "best guesses" for the tie lines.
- FIG. 4 - Solidus portions of the ternary phase diagrams for the Au-In-V's at 25°C. Note that the  $\psi$  phase is supposed to be a high-temperature phase, but it appears to be stable in contact with the other phases in these diagrams.

**TABLE I - Enthalpies of Formation for the Compounds of Au and the Group-III Elements.**

		EXPERIMENTAL	ESTIMATED (Eq.1)
COMPOUND	at. % Au	$\Delta H_{298}^{\circ}(\text{kcal/g-atom})$	$\Delta H_{298}^{\circ}(\text{kcal/g-atom})$
AuAl <sub>2</sub>	33.3	-9.4, <sup>1</sup> -10.1, <sup>4</sup> *	-10.1
AuAl	50.0	-7.8, <sup>1</sup> -9.2 <sup>4</sup>	-9.3
Au <sub>2</sub> Al	66.7	-6.6, <sup>1</sup> -8.3 <sup>4</sup>	-7.1
Au <sub>5</sub> Al <sub>2</sub>	71.4	-5.2 <sup>1</sup>	-6.4
Au <sub>4</sub> Al	78.0, <sup>1</sup> 80.0	-4.7 <sup>1</sup>	-5.0 to -4.6
AuGa <sub>2</sub>	33.3	-5.9 <sup>5</sup> *	-5.9
AuGa	50.0	-5.7 <sup>5</sup>	-5.4
γ, γ'	69.0 to 70.2 <sup>2</sup>		-3.9 to -3.8
β, β'	76.8 to 79.6 <sup>2</sup>		-3.0 to -2.7
AuIn <sub>2</sub>	33.3	-6.0, <sup>6</sup> -5.9 <sup>4</sup> *	-5.9
AuIn	50.0	-5.4, <sup>6</sup> -5.3 <sup>4</sup>	-5.4
ψ	60.5 to 64.6 <sup>3</sup>		-4.8 to -4.3
γ, γ'	68.5 to 71.2 <sup>3</sup>	-3.4 to -3.3 <sup>4</sup>	-4.0 to -3.7
ε, ε'	75.0 to 75.5 <sup>3</sup>		-3.3 to -3.2
ζ <sub>1</sub>	77.5 to 78.3 <sup>3</sup>	-3.1 <sup>4</sup>	-3.0 to -2.9
ζ	77.0 to 87.4 <sup>3</sup>	-3.1 to -1.8 <sup>4</sup>	-3.0 to -1.8
α <sub>1</sub>	85.8 to 89.4 <sup>3</sup>	-2.1 to -1.4 <sup>4</sup>	-1.9 to -1.5
α	87.3 to 100.0 <sup>3</sup>	-1.8 to 0.0 <sup>4</sup>	-1.8 to 0.0

\* For each Au/group-III binary system, the starred value was used as  $\Delta H(X_A^{\circ})$  in Eq.(1).

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Fig 1

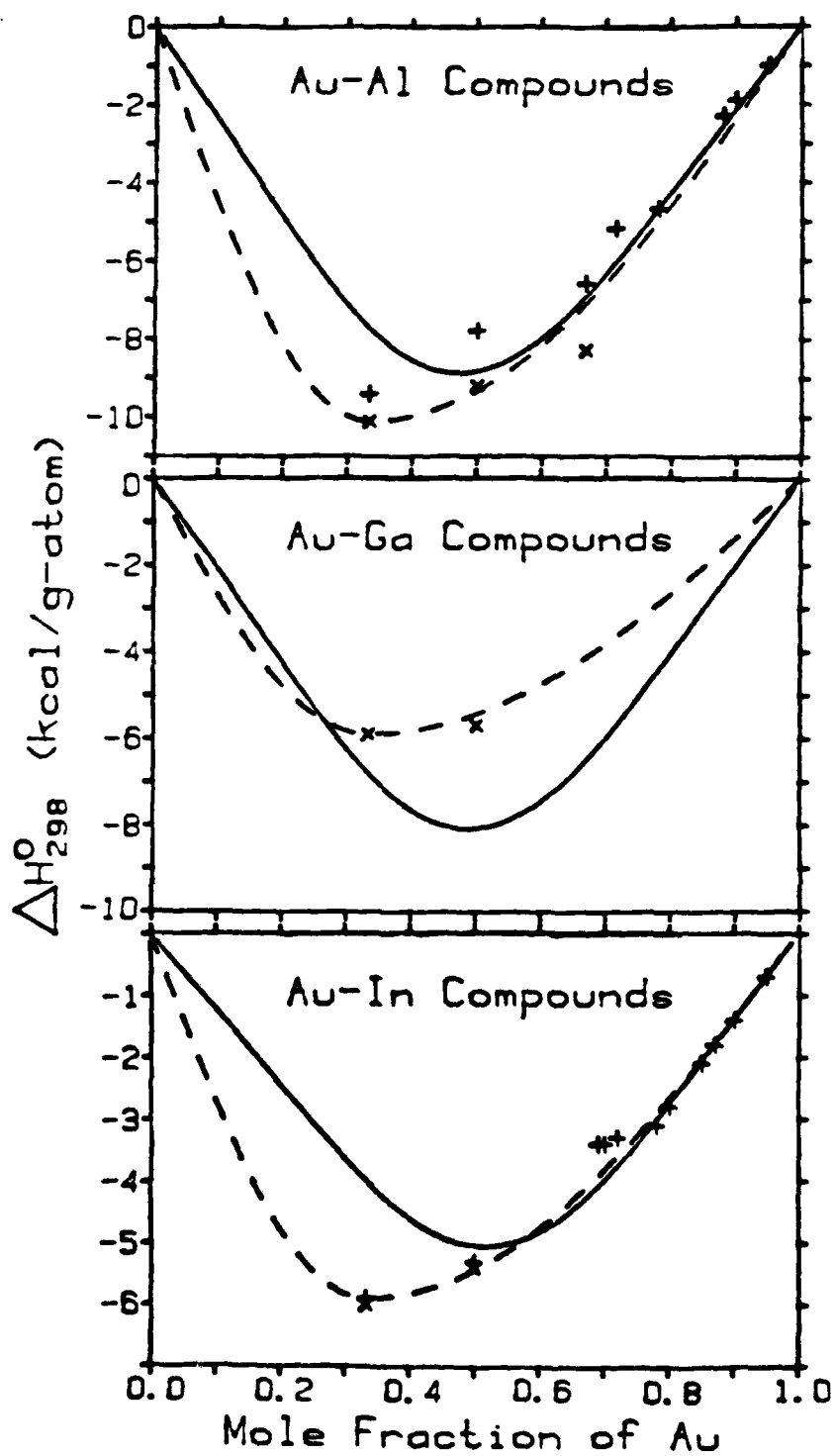


Fig. 2

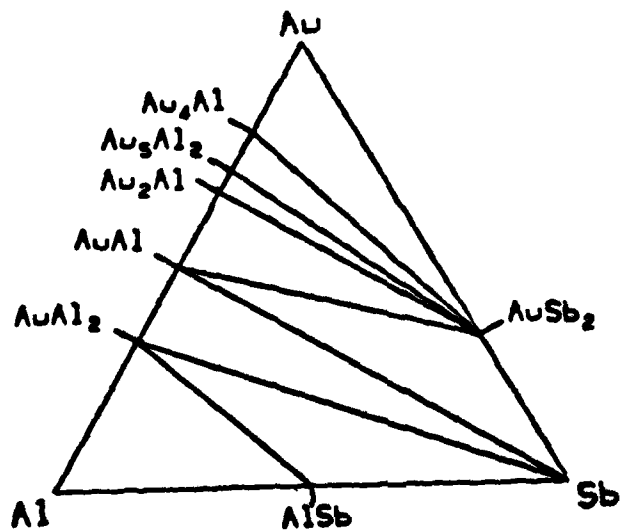
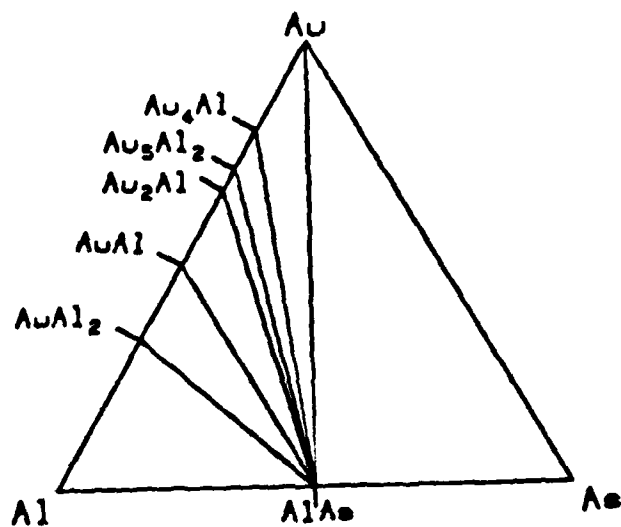
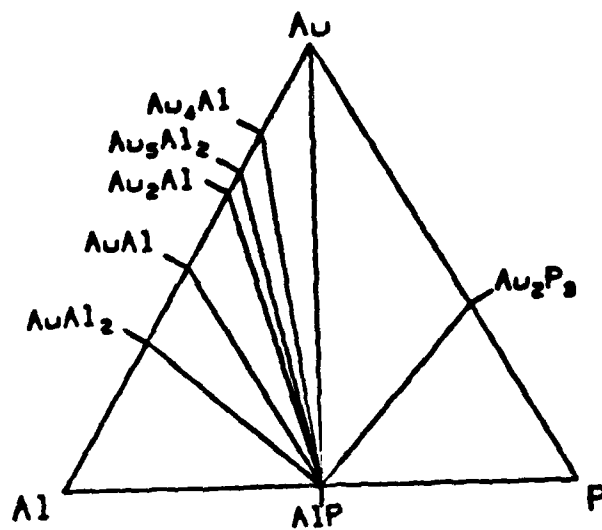


Fig. 3

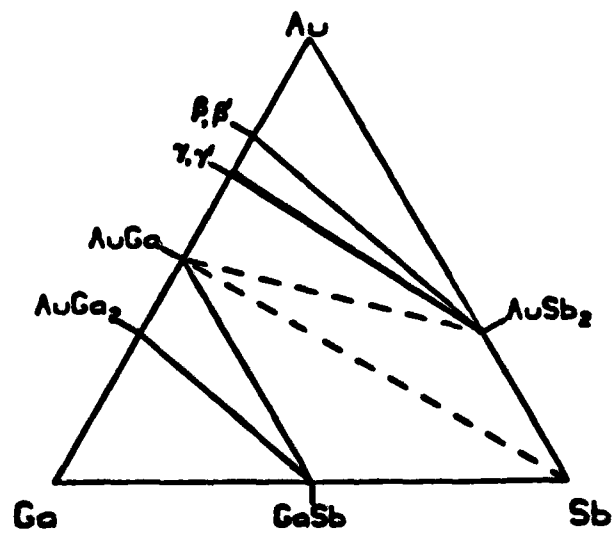
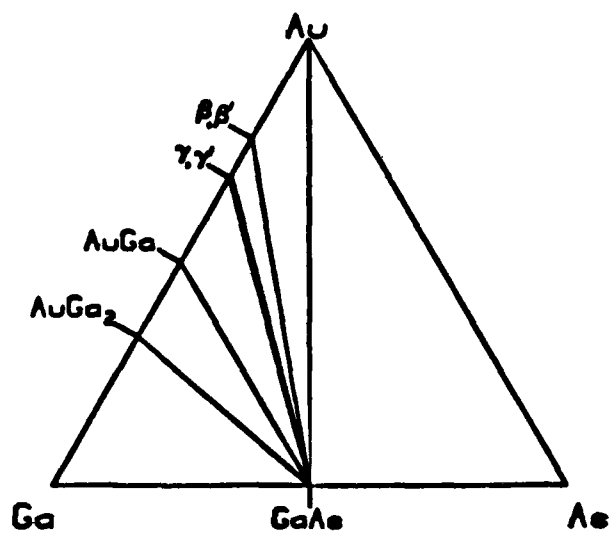
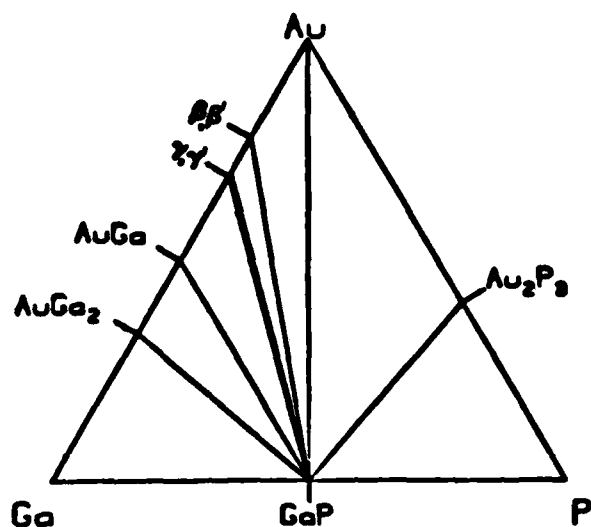
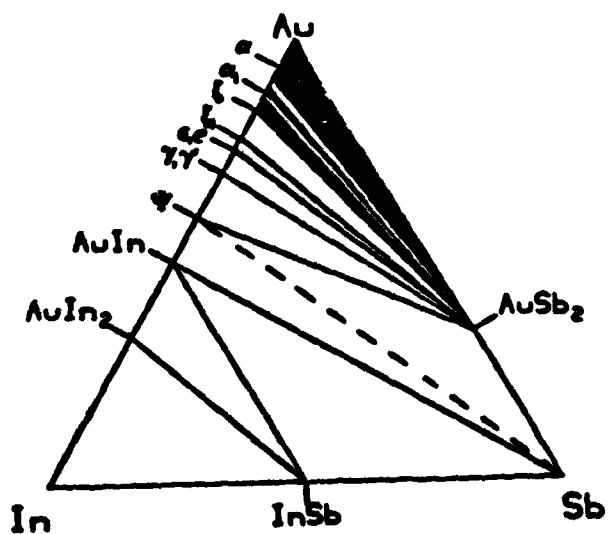
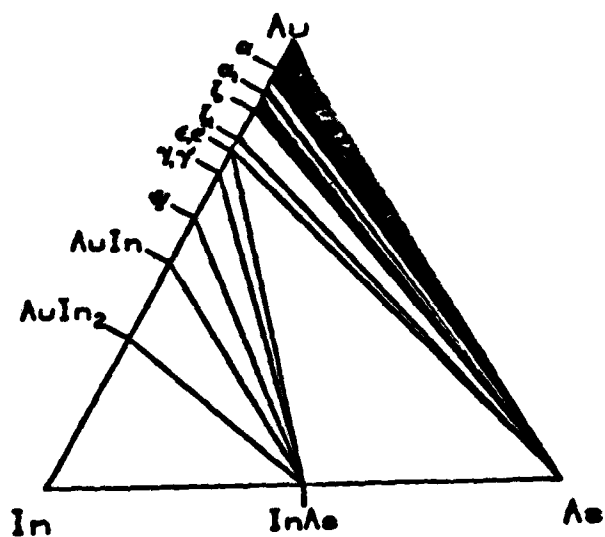
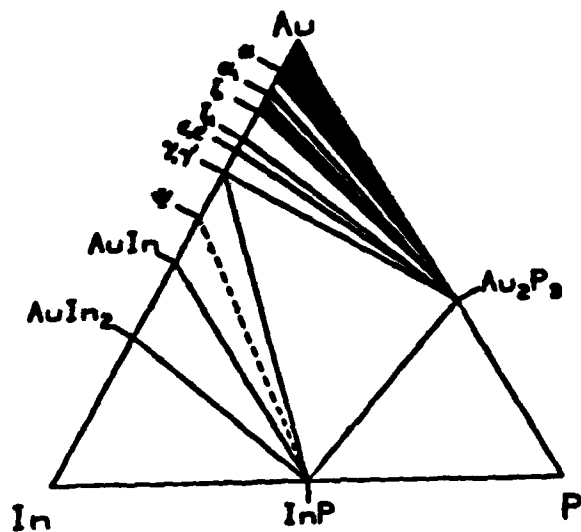


Fig. 4



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